

Subduction fluids and their interaction with the mantle wedge: a perspective from the study of high-pressure ultramafic rocks

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ABSTRACT. — We review three case studies emphasizing the role of ultramafic rocks in the recycling of volatiles and trace elements at convergent plate margins. Serpentinites are major water carriers in subduction zones and their breakdown liberates large quantities of water at sub-arc depths. The incompatible elements incorporated during oceanic serpentinization are released into the fluid phase produced once antigorite dehydrates to olivine + orthopyroxene. Importantly, the antigorite breakdown can trigger either wet melting or production of supercritical fluids in altered basalts and sediments. The produced fluid phases incorporate substantial amounts of incompatible element, initially residing in the crustal reservoirs. The fluid phase which exits the slab is highly reactive with respect to the overlying, silica undersaturated, mantle rocks. This leads to formation of reactive (ortho)pyroxenite layers, which filter the uprising hydrous melt/supercritical fluid to produce aqueous, solute-rich solutions. This fluid has equilibrated with peridotites and is mobile in the mantle.

A consequence of these subduction fluid/mantle reactions is that the mantle wedge domains overlying the slabs can be heterogeneous in composition and layered, due to the presence of reactive pyroxenite

bodies. Another aspect regards the debate whether supercritical fluids or hydrous melts are effective media for trace element transport. Since both agents are saturated in silica, they will react with the silica-undersaturated mantle wedge peridotites to produce aqueous, incompatible trace element-rich residual fluids. Hence, while hydrous melt and/or supercritical fluids are important for scavenging incompatible elements from the slab, they may not be the agents that transfer the metasomatic subduction signature to the inner parts of the mantle wedges.

RIASSUNTO. — Questo contributo riassume tre casi di studio che evidenziano il ruolo delle rocce ultrafemiche nei processi di riciclo delle sostanze volatili e degli elementi in traccia ai margini di placca convergenti. Le serpentiniti sono i sistemi maggiormente responsabili per il trasporto dell'acqua nelle zone di subduzione, dove liberano grandi quantità di acqua a profondità di sub-arco a causa della disidratazione del serpentino. Gli elementi incompatibili incorporati da queste rocce durante l'alterazione oceanica, vengono rilasciati nel fluido prodotto dalla disidratazione del serpentino. L'acqua rilasciata dall'antigorite può innescare la fusione parziale o la formazione di fluidi supercritici nei livelli di rocce basaltiche e meta-sedimentarie costituenti la placca subdotta. I fusi o i fluidi così prodotti incorporano quantità significative di elementi maggiori (oltre il 50 % in peso) e in traccia

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originariamente presenti nelle rocce crostali. La fase fluida rilasciata dallo *slab* subdutto è altamente reattiva rispetto alle soprastanti rocce di mantello e causa la formazione di livelli reattivi a ortopirosseno. Questi livelli ‘filtrano’ i fluidi supercritici e/o i fusi idrati uscenti dallo *slab* per produrre un fluido acquoso residuale ricco in soluto: quest’ultimo si è equilibrato con le peridotiti di mantello ed è in grado di migrare all’interno del *wedge* di mantello. Una conseguenza di queste reazioni fluido/mantello è che i domini del cuneo di mantello soprastanti lo *slab* sono composizionalmente eterogenei e ‘stratificati’ a causa della presenza dei livelli di pirosseniti reattive. Un altro aspetto di queste ricerche riguarda l’efficienza dei fluidi supercritici o dei fusi idrati come agenti di trasporto degli elementi in traccia nel mantello. Entrambi gli agenti sono ricchi in silice e la loro reazione con il mantello libera fluidi acquosi mobili arricchiti in elementi incompatibili. Di conseguenza, mentre i fusi idrati e i fluidi supercritici sono importanti per incorporare elementi dai serbatoi crostali nello *slab*, essi non sono gli agenti che trasferiscono alle parti interne del cuneo di mantello l’impronta metasomatica subduttiva.

INTRODUCTION

Subduction zone fluids play a fundamental role in large-scale mass transfer at convergent plate margins, as they transfer volatiles and incompatible elements from crustal reservoirs in the subducting plates to the overlying mantle. The fluid transport leads to metasomatism of the mantle wedge peridotites and triggers partial melting in regions where peridotites are above the wet solidus temperatures. Based on detailed geochemical studies of arc lavas, it has been inferred that subduction fluids are enriched in large ion lithophile (LILE) and light rare earths (LREE) relative to the high field strength elements (HFSE; McCulloch and Gamble, 1991; Brenan *et al.*, 1994). The crust-to-mantle exchange at subduction zones thus impacts on mantle re-fertilization and is a major driving force for the chemical differentiation of the Earth. The role of fluids in such a cycle has been increasingly emphasized in the last decade and an ongoing debate concerns their nature, composition and effective mobility (Scambelluri and Philippot, 2001; Manning, 2004; Hermann *et al.*, 2006; Zack and John, 2007). The clear

distinction between aqueous fluids and hydrous silicate melts, which characterizes all rock systems at relatively low pressures and temperatures, vanishes at ultrahigh-pressure conditions, where complete miscibility between water and silicate melts has been experimentally attained in a range of P-T conditions and of bulk rock compositions (Bureau and Keppeler, 1999; Stalder *et al.*, 2001; Schmidt *et al.*, 2004; Hermann *et al.*, 2006; Kessel *et al.*, 2005). The existence of a second critical end point, where the wet solidus terminates and a supercritical liquid forms, opened the debate on the role of supercritical fluid phases as metasomatic agents in deep subduction environments.

Studies of natural eclogite-facies rocks provide important constraints to the understanding of deep subduction fluids and their interaction with slab and mantle wedge rocks. The high (HP) and ultrahigh-pressure (UHP) rocks exposed in orogenic terrains provide independent constraints on deep metamorphism in slabs, and represent exceptional natural laboratories on subduction-zone processes in a depth window between 50 and 200 kilometers. Some ultradeep coesite-, diamond- and majorite-bearing rocks preserve primary solid multiphase inclusions (Van Roermund *et al.*, 2002; Stoeckert *et al.*, 2001; Ferrando *et al.*, 2005; Malaspina *et al.*, 2006; Scambelluri *et al.*, 2007), which have been interpreted in some case as remnants of a supercritical fluid phase.

Ultramafic rocks play a fundamental role in volatile and element recycling at convergent plate margins. Field studies have shown that serpentinite is stable at eclogite-facies conditions and hence can transport water into the mantle (Scambelluri *et al.*, 1995). Experiments demonstrate the prolonged stability of antigorite serpentinite to 200 km depth and identify hydrous ultramafic systems as exceptional water carriers into the Earth’s mantle (Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997; Bromiley and Pawley, 2003). These findings have important consequences on subduction dynamics because serpentinites provide a particularly fertile water reservoir for arc magmatism (Ulmer and Trommsdorff, 1995), and because their dehydration can generate intermediate-depth (50–200 Km) earthquakes (Peacock, 2001; Dobson *et al.*, 2002). Serpentinites also act as low density and low viscosity media enabling the exhumation of high and ultrahigh pressure rocks (Hermann *et al.*,

2000; Guillot *et al.*, 2001; Rupke *et al.*, 2004). The mantle domains overlying the subducting plates are other environments where ultramafic rocks play a key role, as the fluid/peridotite interactions at the slab/mantle interface can control the composition of fluids, which are transferred to the inner parts of the mantle wedges. **However, the understanding of mechanisms ruling the slab-to-mantle element transfer is essentially hampered by the paucity of suitable rock samples recording such exchange reactions.** Most studies of supra-subduction zone peridotites investigated either fore-arc xenoliths, or xenoliths sampled at relatively shallow mantle levels, well above arc-magma sources (Vidal *et al.*, 1989; Maury *et al.*, 1992; Laurora *et al.*, 2001). Information on deep metasomatism of the mantle wedge can be gained by studies of HP and UHP terrains, where felsic rocks host metasomatized peridotites (Brueckner, 1998; Rampone and Morten, 2001; Paquin *et al.*, 2004; Scambelluri *et al.*, 2006; Liou *et al.*, 2004). Such associations enable to study the element exchange between crustal and mantle rocks at pressures corresponding to the sub-arc depth of the subducted slab.

To address the role of ultramafic rocks in the fluid and element cycling in subduction zones, here we review three field-based studies concerning fluid release in the slab and possible fluid-rock interactions at a slab-mantle interface. In the first part of this paper we discuss the serpentine dehydration reaction in the slab, and its possible consequences in terms of interaction of de-serpentinization fluids with sedimentary or granitic layers in the slab. In the second part we discuss the case of ultrahigh-pressure garnet orthopyroxenites as proxies for the reaction between mantle peridotites with percolating silicate-rich agents released from felsic and/or metasedimentary slab components.

FLUID PRODUCTION IN SUBDUCTED ULTRAMAFIC ROCKS

Serpentinites are key lithologies in the overall water cycle at oceanic and subduction settings. Several models assume a stratified structure of the slabs (e.g. Poli and Schmidt, 2002), with a lower ultramafic layer, an overlying mafic crust and an uppermost sedimentary layer. This structure can be

inherited from a previous oceanic lithosphere, as documented in present-day fast spreading ridges. In such settings, serpentinization of the oceanic mantle occurs at outer rises, where fractures in the bending plates enhance seawater infiltration at and deep mantle serpentinization (Ranero *et al.*, 2003; Peacock, 2001). Alternatively, part of the layered slab architecture may be erased by tectonic erosion and/or subduction deformation, e.g. boudinage of competent slab layers like the oceanic crust. Also, the lithosphere at slow and ultraslow spreading ridges is not layered, but is characterized by the vast exposure of serpentinized oceanic mantle at the seafloor (Cannat *et al.*, 1995; Dick *et al.*, 2003). During subduction of this type of oceanic lithosphere, serpentinites may be at the top of the slab.

Despite the considerable progress in understanding hydrous phase relations in subducted serpentinites, little is yet known about their geochemical features, particularly about the trace element fingerprints of the fluids released. The only natural cases of analyzed fluids produced during partial to complete breakdown of antigorite at HP to UHP concern the Erro-Tobbio serpentinites (Western Alps) and the chlorite harzburgites from the Betic Cordillera (Southern Spain) (Scambelluri *et al.*, 1997; 2001; 2004a; 2004b; Trommsdorff *et al.*, 1998). The high-pressure serpentinite cycle passes through two dehydration steps (Fig. 1): a minor “brucite-out” reaction leading to the first appearance of metamorphic olivine + antigorite + fluid, and a major fluid release (antigorite-out) related to full antigorite dehydration to olivine + orthopyroxene + fluid. The first reaction is recorded by many Alpine and Betic HP serpentinites (e.g. Liguria: Cimmino *et al.*, 1979; Scambelluri *et al.*, 1995; Zermatt: Li *et al.*, 2004; Monviso: Lombardo *et al.*, 1978; Nevado Filabride: Trommsdorff *et al.*, 1998; Puga *et al.*, 1999). In all these settings the serpentinites are associated with eclogites (Messiga *et al.*, 1995; Messiga *et al.*, 1999; Puga *et al.*, 1999) and display a stable assemblage of olivine + antigorite + Ti-clinohumite + diopside + chlorite, crystallized at 500–650 °C and 2–2.5 GPa. The “brucite-out” reaction (Fig. 1) causes a loss of about 2 wt% bulk water from the initial serpentinites. Best records of this aqueous fluid are primary fluid inclusions hosted by olivine,

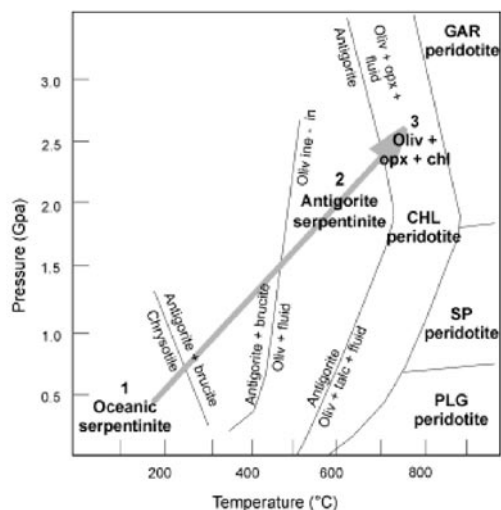


Fig. 1 – Pressure-temperature diagram showing the evolutionary path of the oceanic mantle at the transition from oceanic serpentinites (field 1), to high-pressure antigorite serpentinites (field 2), to olivine-orthopyroxene rocks (field 3). Redrawn after Hermann *et al.* (2000).

diopside and Ti-clinohumite crystallized in veins in the Erro-Tobbio serpentinites (Fig. 2a, b). The inclusions generally display a salt daughter crystal (Fig. 2a), locally associated with ilmenite and magnetite: their salinity can be as high as 50 wt% $\text{NaCl}_{\text{equiv}}$ and the salt composition corresponds to a mixture of $(\text{Na}, \text{K})\text{Cl}$ and MgCl_2 (Scambelluri *et al.*, 1997). Such a composition was taken as evidence for deep recycling of oceanic chlorine and alkalis in the fluid phase (Scambelluri *et al.*, 1997). Lower (present-day) average salinity of 10 wt% NaCl equivalents pertain to primary fluid inclusions present in olivine and diopside in the Betic high-pressure serpentinites (Scambelluri *et al.*, 2001a). The first dehydration fluids released during the serpentinite subduction cycle thus correspond to aqueous solutions which concentrate high amounts of highly incompatible halogen species. The high salinity of such inclusions may reflect changes in the composition of pristine fluids driven by water-consuming processes, such as hydrous mineral crystallization in veins, or hydration of relict (dry) mantle minerals (Scambelluri *et al.*, 1997).

The antigorite breakdown is the second and the most important dehydration reaction in subducted serpentinites (Fig. 1), leading to a bulk loss of 6.5–

12 wt% water. This reaction is recorded by the metamorphic harzburgites of the Betic Cordillera, a unique rock type (Fig. 2c) showing spinifex textured olivine + orthopyroxene (Trommsdorff *et al.*, 1998), as well as coarse granoblastic olivine, orthopyroxene, chlorite \pm Ti-clinohumite. Such metamorphic harzburgites crystallized at 650–700 °C and 2 GPa (Trommsdorff *et al.*, 1998; Puga *et al.*, 1999; Lopez Sanchez-Vizcaino *et al.* 2005) (Fig. 1, Field 3); however, this assemblage can also form at UHP conditions (Ulmer and Trommsdorff, 1995). Olivine and orthopyroxene in these rocks contain primary fluid inclusions filled with solid daughter phases (olivine, magnetite-ilmenite, chlorite, apatite) and an interstitial aqueous liquid. These inclusions are remnants of the fluid phase released at the antigorite breakdown. An initial salinity range of 0.4 – 2 wt% $\text{NaCl}_{\text{equiv}}$ was estimated for this fluid from the bulk-rock net difference of water and chlorine between antigorite serpentinites and harzburgites (Scambelluri *et al.*, 2004a). The trace element compositions of these inclusions were measured by Laser Ablation (LA) ICP MS, using the 0.4 – 2 wt% $\text{NaCl}_{\text{equiv}}$ estimates of the initial fluid salinity as internal standard (Scambelluri *et al.*, 2004a, b). The spider diagram of Fig. 3 shows the trace element compositions of inclusions normalized to the primitive mantle. The fluid inclusions display appreciable incompatible element contents, the highest amounts pertaining to the light elements and the alkalis. In the inclusions, several elements (e.g. Boron) display large variations in the absolute concentrations, which may span over one order of magnitude. All fluid inclusions display comparable patterns, which are systematically enriched in LILE (Rb, Ba, Cs, Sr), B and Li with respect to the HFSE (Ti, Nb). These features are similar to what is observed in arc volcanics (Fig. 3) and are in excellent agreement with experimental results. Tenthorey and Hermann (2004) analyzed fluid compositions that were experimentally produced from the dehydration of serpentinites at high pressure. Their study showed that incompatible elements, which can be taken up during serpentinitization, are fully released during the break down of antigorite.

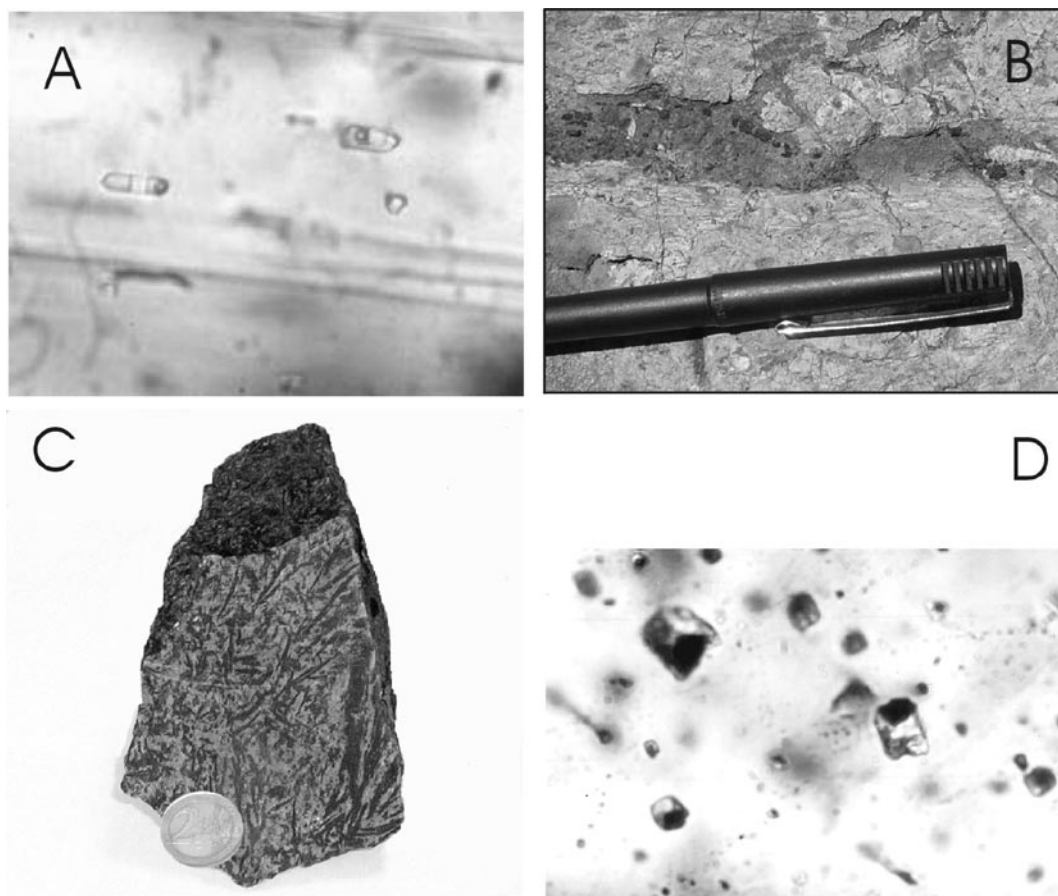


Fig. 2 – A: primary salt-bearing fluid inclusions in diopside from an olivine vein, Erro-Tobbio Unit (Scambelluri *et al.*, 1997). B: olivine, magnetite, diopside and Ti-clinohumite vein in high-pressure serpentinite (Erro Tobbio Unit, Western Alps, Italy). C: Chlorite harzburgite with spinifex-like texture. In light grey is orthopyroxene in brown grey is olivine. (Cerro del Almirez, Bètic Cordillera, Spain; Trommsdorff *et al.*, 1998). D: primary fluid inclusions rich of solid phases (magnetite, olivine chlorite) and with aqueous liquid, in olivine from the chlorite harzburgites (Scambelluri *et al.*, 2001; 2004a).

INTERACTION OF FLUIDS WITH SUBDUCTED SEDIMENTS

Depending on the structure of the subducting lithosphere, the serpentine breakdown fluids may either (i) directly infiltrate the mantle wedge, or (ii) react with crustal rocks of the subducted slab. The first case occurs if the slab is not layered (i.e. slab serpentinites are close to the interface with the mantle wedge) or if the fluid is channelled. This leads to a direct interaction of the antigorite-breakdown fluids with the mantle, which would acquire the signature shown in Fig. 3. The second

case occurs if slabs are layered and crustal rocks are above the serpentinitized oceanic mantle, or are mixed with serpentinite material in mélangé zones at the top of the slab (Spandler *et al.*, 2007). Figure 4 portrays the wet solidus curves for the various slab components (Hermann *et al.*, 2006; Kessel *et al.*, 2006) with the aim to explain the interaction between serpentinite fluids and crustal slab rocks. The wet peridotite solidus reported in Fig. 4 is by Stalder *et al.* (2001), who determined the second critical end point for this system. Also reported in Fig. 4 are the boxes referring to the crystallization conditions of the HP Erro-Tobbio serpentinites, of

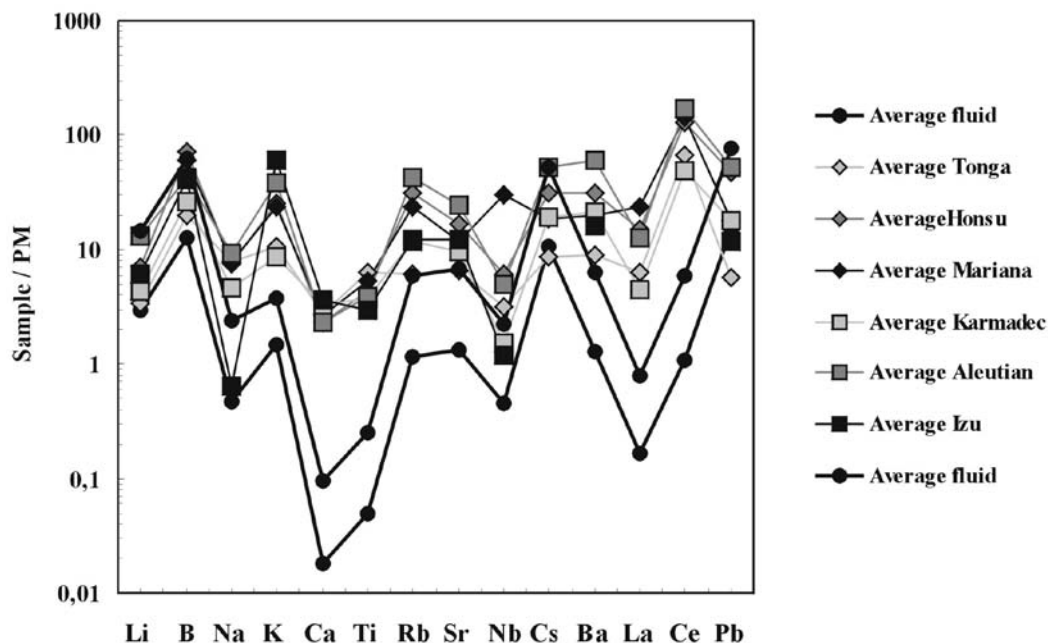


Fig. 3 – Trace element compositions of inclusions in olivine from the chlorite harzburgites (Scambelluri *et al.*, 2004b).

the UHP Cignana ophiolites, and of the HP Bètic harzburgites. All peak conditions are close to the wet solidus and to the second critical endpoint of pelitic and granitic systems. Because of the inverted isotherms in subduction zones, fluids released at 650–700°C during antigorite breakdown will heat up as they rise. As a consequence, these uprising fluids will likely trigger the production of melts or supercritical liquids in the sedimentary layers at 750–800°C (Hermann and Green, 2001). Subducted sediments and altered oceanic crust are the major hosts of incompatible trace elements in the subducted crust (Tenthorey and Hermann, 2004). The great majority of LILE is hosted in phengite in these rock types (Hermann, 2002; Spandler *et al.*, 2003). Because phengite is stable to temperatures of 950–1000°C at sub-arc pressures (Schmidt *et al.* 2004; Hermann and Green, 2001), fluid-absent melting of phengite-bearing metasediments and altered oceanic crust is hardly achieved at sub-arc conditions and it is not regarded to be a viable process to produce LILE enriched slab fluids. In contrast, in the presence of an externally-derived fluid, sediments and altered oceanic crust will undergo fluid-present melting

and LILE will preferentially partition into the fluid phase (Hermann and Green, 2001; Kessel *et al.*, 2005). This demonstrates that fluids liberated from subducted ultramafic rocks play a key role in scavenging trace elements from fertile subduction lithologies such as altered basalts and sediments.

INTERACTION OF SUBDUCTION ZONE FLUIDS WITH THE MANTLE WEDGE

Understanding the interaction of hydrous melts/supercritical fluids with the mantle wedge is crucial to define the volatile and trace element recycling in subduction zones. The garnet orthopyroxenites from the Maowu Ultramafic Complex (Dabie Shan, China) are excellent proxies to unravel the slab-to-mantle element transfer at UHP conditions. This body consists of layered meta-harzburgites, garnet orthopyroxenites and websterites associated with coesite-eclogites. Pyroxenites are locally bounded by phlogopite-rich layers, and are hosted by garnet-coesite-bearing gneisses. In this terrane, gneisses and ultramafic rocks share a common UHP history with peak conditions of 4–6 GPa and

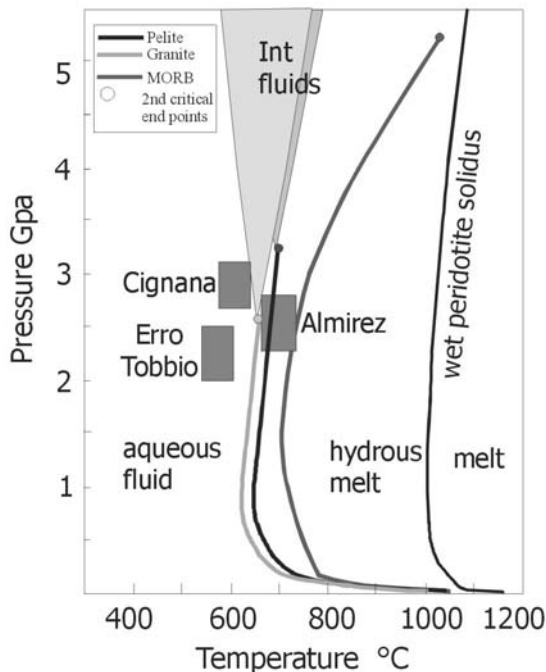


Fig. 4 – Wet solidus curves for ultramafic, mafic, pelitic and granitic systems, showing the second critical end points. The endpoint for ultramafic systems lies at much higher pressures (10 GPa). Boxes refer to the peak P-T conditions for different serpentinite and crustal HP and UHP units of the Alps and of the Betic Cordillera. Redrawn and modified after Hermann *et al.* (2006).

700–750°C (Liou and Zhang, 1998). Although these rocks are not direct samples of a mantle wedge, textural and geochemical data demonstrate that they represent former garnet–peridotites metasomatized by a crust-derived SiO_2 -rich fluid phase at ~ 4.0 GPa and $\sim 750^\circ\text{C}$ (Malaspina *et al.*, 2006). The petrographic observations indicate that the garnet orthopyroxenites preserve a relict paragenesis consisting of olivine + orthopyroxene₁ + garnet₁ \pm clinopyroxene \pm Ti-clinohumite overgrown by coarse-grained orthopyroxene₂ (Fig. 5a, b) associated with porphyroblastic inclusion-rich garnet₂ (Fig. 5c). Orthopyroxene₂ replaces earlier olivine (Fig. 5b) and can include fine-grained garnet₁ and orthopyroxene₁. This indicates that former mantle phases (i.e. olivine, garnet₁ and orthopyroxene₁) were replaced by a Si-enriched phase. The major and trace element compositions of whole-rocks and mineral phases

support the textural evidence that the protolith of these pyroxenites was a peridotite. They display high Mg# and Ni concentrations and chondrite-normalized REE patterns resembling the ones of a depleted mantle (Malaspina *et al.*, 2006). With respect to the inferred harzburgite protholith, however, the Maowu orthopyroxenites are enriched in SiO_2 and Al_2O_3 . LREE enrichment characterizes the bulk rocks as well as the replacive orthopyroxene₂. Such major and trace element compositions of the garnet–orthopyroxenites have been attributed by Malaspina *et al.* (2006) to the infiltration of a metasomatic melt-like fluid phase rich in SiO_2 , Al_2O_3 , and incompatible elements sourced from the country-rock gneisses at peak UHP conditions. Reaction of such a SiO_2 -rich hydrous fluid phase with the peridotite results in a SiO_2 - and Al_2O_3 -loss from the fluid phase to form the garnet orthopyroxenites. On the other hand, part of the H_2O component of the metasomatic agent cannot be accommodated by the newly formed anhydrous phases Opx₂ and Grt₂, and evolves into a residual aqueous fluid. This free fluid is then occasionally trapped by the growing Grt₂ into primary polyphase inclusions (Fig. 5c, d, e, f).

The polyphase inclusions in the Maowu orthopyroxenites therefore provide information on the nature and composition of the residual fluid produced after interaction of the peridotite with the melt-like fluid phase. They display regular negative crystal shapes (Fig. 5c, d, e, f) and contain a solid assemblage (oxide + amphibole + chlorite \pm talc \pm mica \pm apatite) showing constant volume ratios, to suggest that they represent daughter phases that formed from a compositionally homogeneous fluid phase primarily trapped by the UHP garnet. To constrain the nature of such a fluid phase the inclusions have been re-homogenized in a piston cylinder experiment at $P=3.5$ GPa and $T=900^\circ\text{C}$ (Malaspina *et al.*, 2006). The re-homogenization experiment produced a hydrous porous quench, indicating that the UHP fluid in the inclusions was a solute-rich aqueous fluid rather than a hydrous melt. The composition of this fluid has been investigated with LA-ICP-MS analyses performed on the bulk of both polyphase and experimentally re-homogenized inclusions, following the method developed by Heinrich *et al.* (2003). The results give a reliable estimate of the trace element composition of the trapped residual fluid. As shown

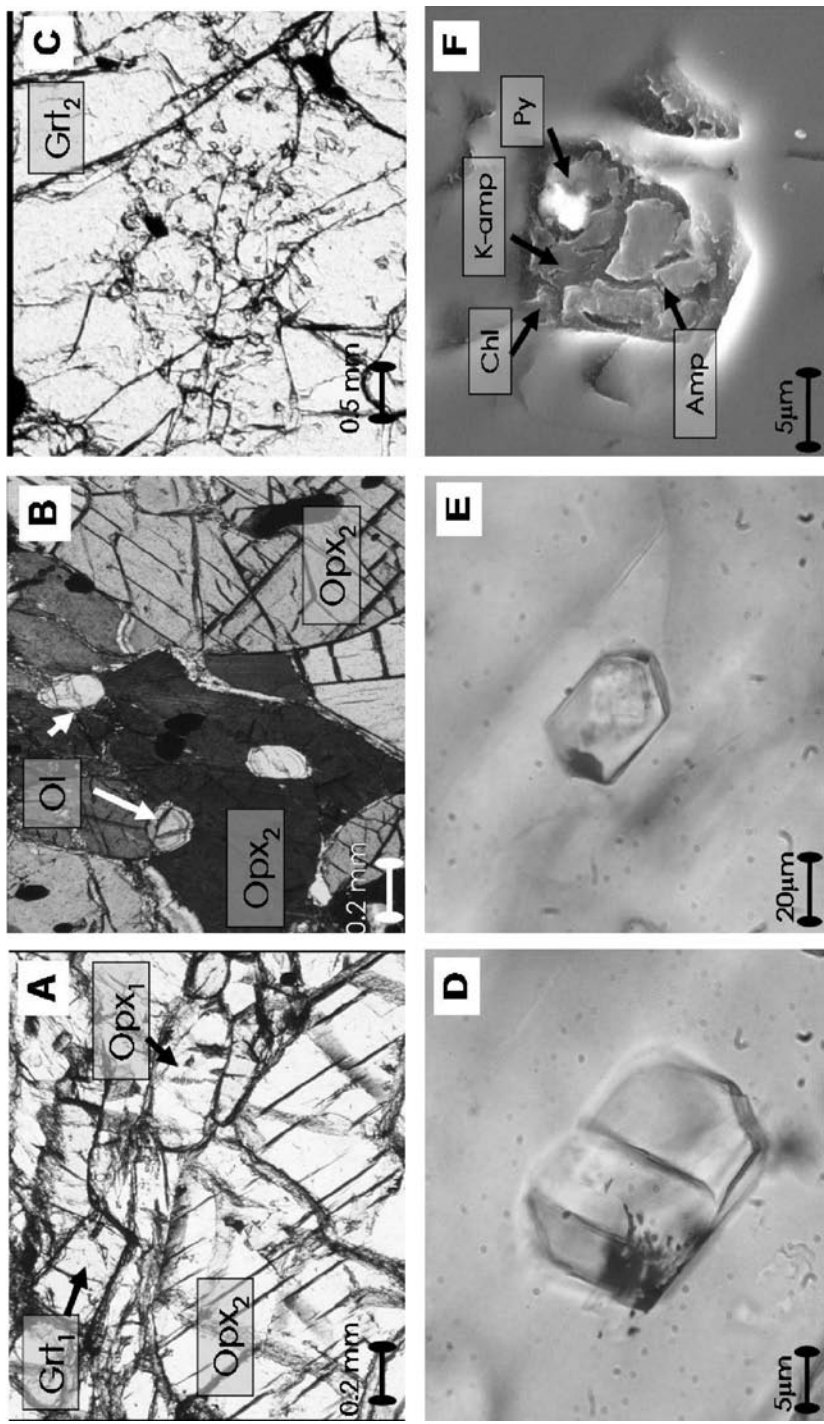


Fig. 5 – Main textures in orthopyroxenites from Maowu, China. A: coarse replacive orthopyroxene (Opx_2) enclosing former garnet (Grt_1) and orthopyroxene (Opx_1). B: blebs of olivine (Ol) replaced by Opx_2 ; C: coarse garnet porphyroblast (Grt_2) with primary solid multiphase inclusions at the core. D, E, F: enlargements of solid multiphase inclusions in garnet porphyroblasts, showing the constancy of volume proportions of mineral inclusions (D, E) and the type of minerals (chlorite; Chl; K-amphibole; K-amp; amphibole; Amp; pyrite; Py) inside the inclusions (F). After Malaspina *et al.* (2006).

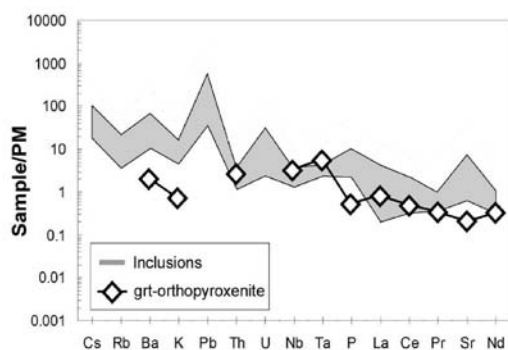


Fig. 6 – Trace element compositions of multiphase inclusions from Maowu orthopyroxenites and of the host rocks. After Malaspina *et al.* (2006).

in Fig. 6, both polyphase and re-homogenized inclusions display very high concentrations of incompatible and fluid-mobile trace elements, with positive spikes in Cs, Ba, Pb, Sr, and a high U–Th ratios. These chemical characteristics provide evidence that the metasomatic agent leading to the formation of the orthopyroxenites had a crustal affinity. The residual aqueous fluid retained most of the incompatible elements that were present in the reacting hydrous-melt. In fact, the whole-rock composition, represented by the white diamonds in Fig. 6, shows relative enrichments only in LREE, whereas most of the fluid-mobile elements are below the detection limit. The reason for this observation is that the rock-forming minerals – orthopyroxene and garnet – are not able to incorporate these incompatible elements. The low LILE contents in the whole-rocks imply that such LILE-enriched fluid largely escaped the system and was only occasionally trapped in garnet₂ to form the polyphase inclusions. This fluid is able to migrate up into the mantle where it may enhance crystallization of metasomatic amphibole (below 3 GPa; Fumagalli and Poli, 2005) and/or phlogopite, to ultimately reach the locus of partial melting in the mantle wedge.

DISCUSSION AND CONCLUSIONS

The presented case studies highlight the importance of ultramafic rocks in the recycling of volatiles and trace elements at convergent plate margins. Serpentinites are the main carriers

of water in subduction zones and the breakdown of antigorite liberates large quantities of water at sub-arc depths. Moreover, incompatible elements incorporated during oceanic serpentinization will be released into the HP-UHP fluid phase once antigorite breaks down. Probably the most important effect on the trace element recycling in subduction zones is that fluids derived from the antigorite breakdown will trigger wet melting in altered basalts and sediments. The produced melts/supercritical fluids incorporate substantial amounts of incompatible elements, initially residing in the crustal reservoirs. Fig. 7 describes a possible deep subduction environment, where the aqueous fluids released by the serpentinites infiltrate an overlying meta-sedimentary layer to enhance either its partial melting or the production of silicate-rich fluids. The fluid phases that exit the slab will be highly reactive to the surrounding mantle peridotites. This will produce the orthopyroxenite layers described in the Maowu examples and filter the uprising hydrous melt-supercritical fluid phase. The fluid uprising from such filtering zone will be an aqueous, solute-rich solution with composition comparable with the one portrayed in Fig. 6. This fluid equilibrated with mantle rocks through the filtering process and is mobile in the mantle.

A first implication of our case studies thus concerns the mantle wedges above subducting slabs, which can be heterogeneous in composition and layered, due to the presence of reactive pyroxenite bodies. Si-enrichment in the mantle was claimed by previous studies of supra-subduction mantle domains affected by re-fertilization and/or formation of reactive pyroxenites (Kelemen *et al.*, 1998; Yaxley and Green, 1998; Garrido and Bodinier, 1999; Groove *et al.*, 2005). Also, Sobolev *et al.* (2005) proposed that interaction between recycled crust and mantle peridotites produces pyroxenites in the deep mantle, and melting of such a mantle might contribute to the genesis of ocean island basalts. Here we have detailed a feasible mechanism by which the supra-subduction mantle reacts with slab-derived silicate agents to produce large zones where pyroxenites dominate.

One interesting aspect of this work is that the debate whether trace elements are transported in supercritical fluids or hydrous melts is after all not that essential. Because both these agents are saturated in silica, they will inevitably react with

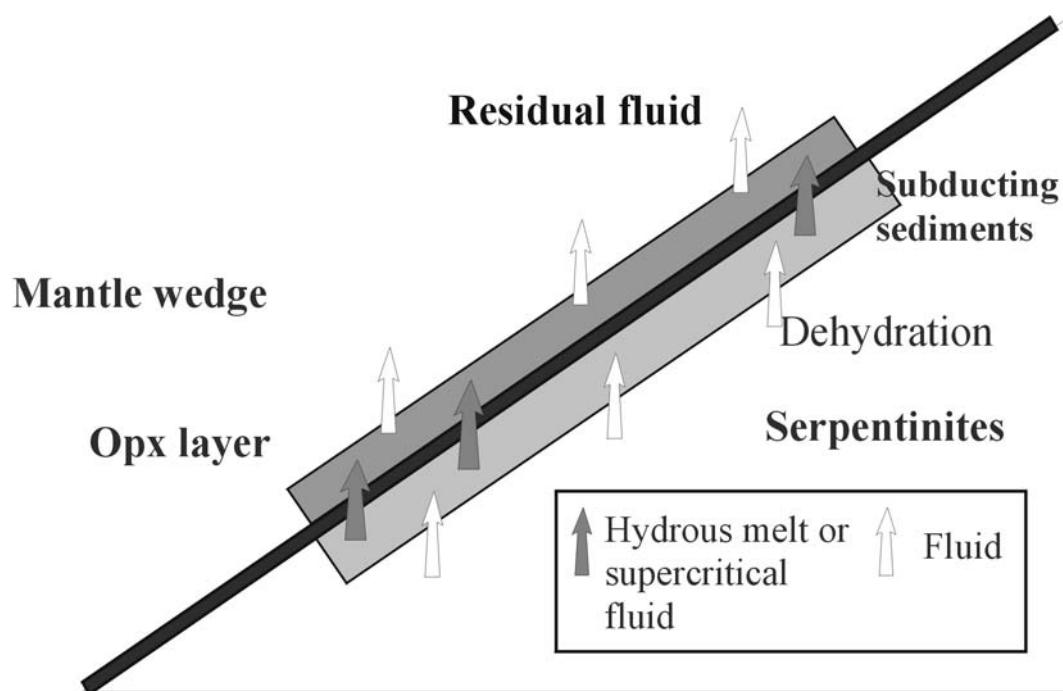


Fig. 7 – Model for fluid evolution. See the text for explanation. Redrawn after Scambelluri *et al.* (2006)

the silica-undersaturated mantle wedge as outlined in the Maowu case study. During this reaction the fluid phase will be transformed, as Si and Al are extracted from the melt/supercritical fluid, leaving an aqueous, incompatible trace element enriched residual fluid. Hence, while hydrous melt and/or supercritical fluids are important for scavenging incompatible elements from the slab, they are unlikely the agents that transport the metasomatic trace element signature to the source of the arc magmas. Only in the case that the released fluids are channelled in pyroxenite dikes in the mantle wedge, the reaction with mantle olivine would be inhibited and the slab-derived Si- and trace element-rich liquids might migrate into overlying hotter regions of the mantle wedge.

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REFERENCES

- BRENAN J.M., SHAW H.F., RYERSON F.J. and PHINNEY D.L. (1995) - *Mineral-aqueous fluid partitioning of trace elements at 900°C and 2.0 GPa: constraints on the trace element chemistry of mantle and deep crustal fluids*. *Geochim. Cosmochim. Acta*, **59**, 3331–3350.
- BUREAU H. and KEPPLER H. (1999) - *Complete miscibility between silicate melts and hydrous fluids in the upper mantle: experimental evidence and geochemical implications*. *Earth Planet. Sci. Lett.*, **165**, 187–196.
- BROMILEY G.D. and PAWLEY A. (2003) - *The stability of antigorite in the systems MgO-SiO₂-H₂O (MSH) and MgO-Al₂O₃-SiO₂-H₂O (MASH): the effects of*

- Al^{3+} substitution on high-pressure stability. *Am. Mineral.*, **88**, 99-108.
- BRUECKNER H.K. (1998) - A sinking intrusion model for the introduction of garnet-bearing peridotites into continent collision orogens. *Geology*, **26**, 631-634.
- LI X.P., ZHANG L., WEI C., AI Y. and CHEN J. (2007) - Petrology of rodingite derived from eclogite in western Tianshan, China. *J. Metam. Geol.*, **25**, 363-382.
- CANNAT M., MÉVEL C., MAIA M., DEPLUS C., DURAND C., GENTE P., AGRINIER P., BELAROUCHI A., DUBUISSON G., HUMLER E. and REYNOLDS J. (1995) - Thin crust, ultramafic exposures and rugged faulting patterns at the Mid-Atlantic Ridge (22°-24°N). *Geology*, **23**, 49-52.
- CIMMINO F., MESSIGA B. and PICCARDO G.B. (1979) *Ti-clinohumite-bearing assemblages within antigoritic serpentinites of the Voltri Massif (Western Liguria): inferences on the geodynamic evolution of piemontese ultramafic sections*. *Ofioliti*, **4**, 97-120.
- DICK H.J.B., LIN J. and SCHOUTEN H. (2003) - An ultraslow-spreading class of ocean ridge. *Nature*, **426**, 405-412.
- DOBSON D.P., MEREDITH P.G. and BOON S.A. (2002) - Simulation of subduction zone seismicity by dehydration of serpentine. *Science*, **298**, 1407-1410.
- FERRANDO S., FREZZOTTI M.L., DALLAI L. and COMPAGNONI R. (2005) - Multiphase solid inclusions in UHP rocks (Su-Lu, China): remnants of supercritical silicate-rich aqueous fluids released during continental subduction. *Chem. Geol.*, **223**, 68-81.
- FUMAGALLI P. and POLI S. (2005) - Experimentally determined phase relations in hydrous peridotites to 6.5 gpa and their consequences on the dynamics of subduction zones. *J. Petrol.*, **46**, 555-578.
- GARRIDO C.J. and BODINIER J.L. (1999) - Diversity of mafic rocks in the Ronda peridotite: Evidence for pervasive melt-rock reaction during heating of subcontinental lithosphere by upwelling asthenosphere. *J. Petrol.*, **40**, 729-754.
- GROVE T.L., BAKER M.B., PRICE R.C., PARMAN S.W., ELKINS-TANTON L.T., CHATTERJEE N. and MÜNTENER O. (2005) - Magnesian andesite and dacite lavas from Mt. Shasta, northern California: products of fractional crystallization of H₂O-rich mantle melts. *Contrib. Mineral. Petrol.*, **148**, 542-565.
- GUILLOT S., HATTORI K. H., DE SIGOYER J., NÄGLER T. and AUZENDE A.L. (2001) - Evidence of hydration of the mantle wedge and its role in the exhumation of eclogites. *Earth and Planet. Sci. Lett.*, **193**, 115-127.
- HEINRICH C.A., PETTKE T., HALTER W.E., AIGNER-TORRES M., AUDÉTAT A., GÜNTHER D., HATTENDORF B., BLEINER D., GUILLONG M. and HORN I. (2003) - Quantitative multi-element analysis of minerals, fluid and melt inclusions by laser-ablation inductively-coupled-plasma mass spectrometry. *Geochim. Cosmochim. Acta*, **67**, 3473-3497.
- HERMANN J., MÜNTENER O. and SCAMBELLURI M. (2000) - The importance of serpentinite mylonites for subduction and exhumation of oceanic crust. *Tectonophysics*, **327**, 225-238.
- HERMANN J. and GREEN D.H. (2001) - Experimental constraints on high pressure melting in subducted crust. *Earth Planet. Sci. Lett.*, **188**, 149-168.
- HERMANN J. (2002) - Allanite: Thorium and light rare earth element carrier in subducted crust. *Chem. Geol.*, **192**, 289-306.
- HERMANN J., SPANDLER C., HACK A. and KORSAKOV A.V. (2006) - Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: Implications for element transfer in subduction zone. *Lithos*, **92**, 399-417.
- KELEMEN P.B., HART S.R. and BERNSTEIN S. (1998) - Silica enrichment in the continental upper mantle via melt/rock reaction. *Earth. Planet. Sci. Lett.*, **164**, 387-406.
- KESSEL R., SCHMIDT M.W., ULMER P. and PETTKE T. (2005) - Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120-180 km depth. *Nature*, **437**, 724-727.
- LAURORA A., MAZZUCHELLI M., RIVALENTI G., VANNUCCI R., ZANETTI A., BARBIERI M.A. and CINGOLANI C.A. (2001) - Metasomatism and melting in carbonated peridotite xenoliths from the mantle wedge: the Gobernador Gregores case (Southern Patagonia). *J. Petrol.*, **42**, 69-87.
- LI X.P., M. RAHN and K. BUCHER (2004) - Serpentinites of the Zermatt-Saas ophiolite complex and their texture evolution. *J. Metam. Geol.*, **22**, 159-177.
- LIU J.G., TSUJIMORI T., ZHANG R.Y., KATAYAMA I. and MARUYAMA S. (2004) - Global UHP Metamorphism and Continental Subduction/Collision: the Himalayan Model. *Int. Geol. Rev.*, **46**, 1-27.
- LIU J.G. and ZHANG R.Y. (1998) - Petrogenesis of an ultrahigh-pressure garnet-bearing ultramafic body from Maowu, Dabie Mountains, east-central China. *Isl. Arc.*, **7**, 115-134.
- LOMBARDO B., NERVO R., COMPAGNONI R., MESSIGA B., KIENAST J.R., MEVEL C., FIORA L., PICCARDO G.B. and LANZA R. (1978) - Osservazioni preliminari sulle ofioliti del Monviso (Alpi Occidentali). *Rend.*

- Soc. It. Mineral. Petrol., **34**, 253-305.
- LOPEZ SANCHEZ-VIZCAINO V., TROMMSDORFF V., GOMEZ-PUGNAIRE M.T., GARRIDO C.J., MÜNTENER O. and CONNOLLY J.A.D. (2005) - *Petrology of titanian clinohumite and olivine at the high-pressure breakdown of antigorite serpentinite to chlorite harzburgite (Almirez Massif, S. Spain)*. *Contrib. Mineral. Petrol.*, **149**, 627-646.
- MALASPINA N., HERMANN J., SCAMBELLURI M. and COMPAGNONI R. (2006) - *Polyphase inclusions in garnet-orthopyroxenite (Dabie Shan, China) as monitors for metasomatism and fluid-related trace element transfer in subduction zone peridotite*. *Earth Planet. Sci. Lett.*, **249**, 173-187.
- MANNING C.E. (2004) - *The chemistry of subduction zone fluids*. *Earth Planet. Sci. Lett.*, **223**, 1-16.
- MAURY R.C., DEFANT M.J. and JORON J.L. (1992) - *Metasomatism of the subarc mantle inferred from trace elements in Philippine xenoliths*. *Nature*, **360**, 661-663.
- McCULLOCH M.T. and GAMBLE A.J. (1991) - *Geochemical and geodynamical constraints on subduction zone magmatism*. *Earth Planet. Sci. Lett.*, **102**, 358-374.
- MESSIGA B., SCAMBELLURI M. and PICCARDO G.B. (1995) - *Formation and breakdown of chloritoid-omphacite high-pressure assemblages in mafic systems: evidence from the Erro-Tobbio eclogitic metagabbros (Ligurian Western Alps)*. *Eur. J. Mineral.*, **7**, 1149-1167.
- MESSIGA B., KIENAST J.R., REBAY G., RICCARDI M.P. and TRIBUZIO R. (1999) - *Cr-rich magnesio chloritoid eclogites from the Monviso ophiolites (Western Alps, Italy)*. *J. Metam. Geol.*, **17**, 287-299.
- PAQUIN J., ALTHERR R. and LUDWIG T. (2004) - *Li-Be-B systematics in the ultrahigh-pressure garnet peridotite from Alpe Arami (Central Swiss Alps): implications for slab-to-mantle wedge transfer*. *Earth Planet. Sci. Lett.*, **218**, 507-519.
- PEACOCK S. (2001) - *Are the lower planes of double seismic zones caused by serpentine dehydration in subducting oceanic mantle?* *Geology*, **29**, 299-302.
- POLI S. and SCHMIDT M.W. (2002) - *Petrology of subducted slabs*. *Ann. Rev. Earth Planet. Sci.*, **30**, 207-235.
- PUGA E., NIETO J.M., DÍAZ DE FEDERICO A., BODINIER J.L. and MORTEN L. (1999) - *Petrology and metamorphic evolution of ultramafic rocks and dolerite dykes of the Betic Ophiolitic Association (Mulhacén Complex, SE Spain): Evidence of eo-Alpine subduction following and ocean-floor metasomatic process*. *Lithos*, **49**, 23-56.
- RAMPONE E. and MORTEN L. (2001) - *Records of crustal metasomatism in the garnet peridotites of the Ulten Zone (Upper Austroalpine, Eastern Alps)*. *J. Petrol.*, **42**, 207-219.
- RANERO C.R., PHIPPS MORGAN J., MCINTOSH K. and REICHERT C. (2003) - *Bending-related faulting and mantle serpentinization at the Middle America trench*. *Nature*, **425**, 367-373.
- VAN ROERMUND H.L.M., CARSWELL D.A., DRURY M.R. and HEIJBOERT T.C. (2002) - *Microdiamonds in a megacrystic garnet websterite pod from Bardane on the island of Fjortoft, western Norway: evidence for diamond formation in mantle rocks during deep continental subduction*. *Geology*, **30**, 959-962.
- RUPKE L.H., PHIPPS-MORGAN J., HORT M. and CONNOLLY J.A.D. (2004) - *Serpentine and the subduction zone water cycle*. *Earth Planet. Sci. Lett.*, **223**, 17-34.
- SCAMBELLURI M., MÜNTENER O., HERMANN J., PICCARDO G.B. and TROMMSDORFF V. (1995) - *Subduction of water into the mantle: History of an alpine peridotite*. *Geology*, **23**, 459-462.
- SCAMBELLURI M. and PHILIPPOT P. (2001) - *Deep fluids in subduction zones*. *Lithos*, **55**, 213-227.
- SCAMBELLURI M., PICCARDO G.B., PHILIPPOT P., ROBBIANO A. and NEGRETTI L. (1997) - *High salinity fluid inclusions formed from recycled seawater in deeply subducted alpine serpentinite*. *Earth Planet. Sci. Lett.*, **148**, 485-500.
- SCAMBELLURI M., BOTTAZZI P., TROMMSDORFF V., VANNUCCI R., HERMANN J., GÓMEZ-PUGNAIRE M.T. and LÓPEZ-SÁNCHEZ VIZCAINO V. (2001a) - *Incompatible element-rich fluids released by antigorite breakdown in deeply subducted mantle*. *Earth Planet. Sci. Lett.*, **192**, 457-470.
- SCAMBELLURI M., RAMPONE E. and PICCARDO G.B. (2001b) - *Fluid and element cycling in subducted serpentinite: A trace element study of the Erro-Tobbio high-pressure ultramafites (Western Alps, NW Italy)*. *J. Petrol.*, **42**, 55-67.
- SCAMBELLURI M., MÜNTENER O., OTTOLINI L., PETTKE T. and VANNUCCI R. (2004a) - *The variability of B, Cl and Li in the subducted oceanic mantle and in the antigorite-breakdown fluids: implications for fluid processes and light element recycling*. *Earth Planet. Sci. Lett.*, **222**, 217-234.
- SCAMBELLURI M., FIEBIG J., MALASPINA N., MÜNTENER O. and PETTKE T. (2004b) - *Serpentinization: Implications for fluid processes and trace-element recycling*. *Int. Geol. Rev.*, **46**, 595-613.
- SCAMBELLURI M., HERMANN J., MORTEN L. and RAMPONE E. (2006) - *Melt- versus fluid-induced metasomatism in spinel to garnet wedge*

- peridotites (Ulten Zone, Eastern Italian Alps): clues from trace element and Li abundances. Contrib. Mineral. Petrol.*, **151**, 372–394.
- SCAMBELLURI M., PETTKE T. and VAN ROERMUND H.L.M. (2007) - *Majoritic garnets monitor deep subduction fluid flow and mantle dynamics. Geology*, in press.
- SCHMIDT M.W., VIELZEUF D. and AUZANNEAU E. (2004) - *Melting and dissolution of subducting crust at high pressures: the key role of white mica. Earth Planet. Sci. Lett.*, **228**, 65–84.
- SPANDLER C., HERMANN J., ARCULUS R. and MAVROGENES J. (2003) - *Redistribution of Trace Elements during Prograde Metamorphism from Lawsonite Blueschist to Eclogite Facies; Implications for Deep Subduction-zone Processes. Contrib. Mineral. Petrol.*, **146**, 205–222.
- SPANDLER C., HERMANN J., FAURE K., MAVROGENES J.A. and ARCULUS R.J. (2007) - *The importance of talc-chlorite “hybrid” rocks for volatile recycling through subduction zones: evidence from the high-pressure subduction mélange of New Caledonia. Contrib. Mineral. Petrol.* DOI 10.1007/s00410-007-0236-2.
- SOBOLEV A.V., HOFMANN A.W., SOBOLEV S.V. and NIKOSIAN I.K. (2005) - *An olivine-free mantle source of Hawaiian shield basalts. Nature*, **434**, 590–597.
- STALDER R., ULMER P., THOMPSON A. and GÜNTHER D. (2001) - *High-Pressure fluids in the system MgO-SiO₂-H₂O under upper mantle conditions. Contrib. Mineral. Petrol.*, **140**, 607–618.
- STOEKERT B., DYSTER J., TREPAN C. and MASONNE H.J. (2001) - *Microdiamond daughter crystals precipitated from supercritical COH + silicate fluids included in garnet, Erzgebirge, Germany. Geology*, **29**, 391–394.
- TENTHOREY E. and HERMANN J. (2004) - *Composition of fluids during serpentinite breakdown in subduction zones: evidence for limited boron mobility. Geology*, **32**, 865–868.
- TROMMSDORFF V., LÓPEZ-SÁNCHEZ VIZCAINO V., GÓMEZ-PUGNAIRE M.T. and MÜNTENER O. (1998) - *High pressure breakdown of antigorite to spinifex-textured olivine and orthopyroxene, SE Spain. Contrib. Mineral. Petrol.*, **132**, 139–148.
- ULMER P. and TROMMSDORFF V. (1995) - *Serpentine stability to mantle depths and subduction-related magmatism. Science*, **268**, 858–861.
- ULMER P. and TROMMSDORFF V. (1999) - *Phase relations of hydrous mantle subducting to 300 km. In: Mantle Petrology: Field observations and high pressure experimentation: A tribute to Francis R. (Joe) Boyd. Geochemical Society Special Publication No. 6: 259–281*
- VIDAL P.H., DUPUY C., MAURY R. and RICHARD M. (1989) - *Mantle metasomatism above subduction zones: trace-element and radiogenic isotope characteristics of peridotite xenoliths from Batan Island (Philippines). Geology*, **17**, 1115–1118.
- WUNDER B. and SCHREYER W. (1997) - *Antigorite: High pressure stability in the system MgO-SiO₂-H₂O (MSH). Lithos*, **41**, 213–227.
- YAXLEY G.M. and GREEN D.H. (1998) - *Reactions between eclogite and peridotite: Mantle refertilisation by subduction of oceanic crust. Schweiz. Mineral. Petrogr. Mitt.*, **78**, 243–255.
- ZACK T. and JOHN T. (2007) - *An evaluation of reactive fluid flow and trace element mobility in subducting slabs. Chem Geol.*, **239**, 199–216.

